

Electronic structures of B-2p and C-2p of boron-doped diamond film by soft X-ray absorption and emission spectroscopy

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(Dated: submitted to Phys. Rev. B, June 14 2004)

X-ray absorption (XAS) and emission (XES) spectroscopy near B-K and C-K edges have been performed on metallic ($\sim 1\text{at\%}$ B, B-diamond) and semiconducting ($\sim 0.1\text{at\%}$ B and N, BN-diamond) doped-diamond films. Both B-K XAS and XES spectra shows metallic partial density of state (PDOS) with the Fermi energy of 185.3 eV, and there is no apparent boron-concentration dependence in contrast to the different electric property. In C-K XAS spectrum of B-diamond, the impurity state ascribed to boron is clearly observed near the Fermi level. The Fermi energy is found to be almost same with the top of the valence band of non-doped diamond, E_V , 283.9 eV. C-K XAS of BN-diamond shows both the B-induced shallow level and N-induced deep-and-broad levels as the in-gap states, in which the shallow level is in good agreement with the activation energy ($E_a=0.37$ eV) estimated from the temperature dependence of the conductivity, namely the change in C-2p PDOS of impurity-induced metallization is directly observed. The electric property of this diamond is mainly ascribed to the electronic structure of C-2p near the Fermi level. The observed XES spectra are compared with the DVX α cluster calculation. The DVX α result supports the strong hybridization between B-2p and C-2p observed in XAS and XES spectra, and suggests that the small amount of borons ($\leq 1\text{at\%}$) in diamond occupy the substitutional site rather than interstitial site.

PACS numbers: 81.05.Uw, 71.55.-i, 74.25.Jb, 78.70.En, 78.70.Dm

I. INTRODUCTION

Diamond is a very attractive material with industrial applications because of its maximum hardness, high surface stability (chemical inertness), large energy gap (~ 5.5 eV), high thermal conductivity, and so on. Boron-doped diamond expands its possibility into an application of electric devices.[1] Lightly boron-doped diamond shows *p*-type character with an activation energy of about 0.37 eV,[2] and heavily doped diamond shows metallic conductivity.[3] Furthermore the recent discovery of the superconductivity of more-heavily boron doped diamond brought a new attention to the problem in the superconductivity of impurity-induced metallization in semiconductor.[4] However the crystallinity of these heavily doped compounds is not clear in contrast to the low ($\leq 0.5\%$) doped diamonds. It seems that boron atoms occupy the interstitial sites when heavily doped case ($\sim 4\%$)[5, 6] and substitute for carbon at low doped case ($\leq 0.5\%$).[7] It should be important to clarify the memorable electronic structure of more-heavily doped diamonds, but at present the priority study should be that of the low doped diamond due to their crystallinities. Therefore, in this paper, we study the electronic struc-

tures of low doped diamond with the metallic ($\sim 1\text{at\%}$) and semiconducting ($\sim 0.1\text{at\%}$) characters. The partial density of states (PDOS's) of boron- and carbon-2p using X-ray absorption (XAS) and X-ray emission (XES) spectroscopy near the B-K and C-K edges of these doped diamonds are reported. XAS and XES near B-K and C-K edges are powerful techniques for direct measurement of PDOS's of dopant-boron and host-carbon, especially for the semiconducting or insulating materials, in comparison with the electron spectroscopy.

II. EXPERIMENTAL

Highly boron-doped diamond thin films were deposited on Si (100) wafers in a microwave plasma-assisted chemical vapor deposition (MPCVD) system (ASTeX Corp.). Details of the preparation were described elsewhere.[8] A mixture of acetone and methanol in the volume ratio of 9/1 was used as the carbon source. B_2O_3 , the boron source, was dissolved in the acetone-methanol solution at a B/C atomic ratio of 1:100. This 1 at% boron-doped diamond, B-diamond, shows metallic conductivity at the room temperature. The lightly doped diamond film is synthesized using MPCVD method with a *h*-BN target

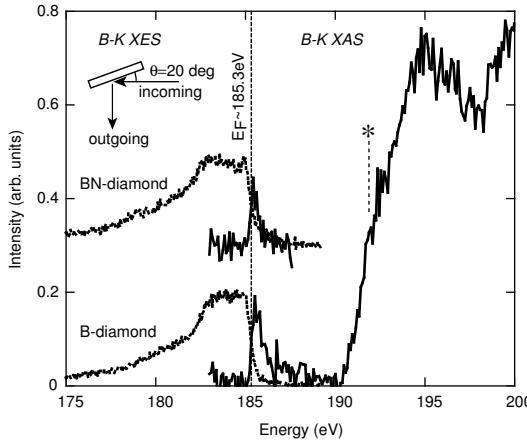


FIG. 1: B-K XAS and XES spectra of B- and BN-diamonds. The incident angle was set to $\theta=20^\circ$. The excitation energy of XES measurement was 200 eV.

(BN-diamond).[9] The boron and nitrogen concentrations are estimated to be 0.1at% for both boron and nitrogen by SIMS measurements. And the electric property is semiconducting with the activation energy E_a of about 0.37 eV.[9] However the value of E_a depends on the impurity concentration, this value is consistent with the previous reports of lightly boron-doped diamond film.[1, 7] Several values of the nitrogen-impurity levels (deep n -type) are reported.[10]

Soft X-ray absorption (XAS) and XES measurements were performed at BL-8.0.1[11] of the Advanced Light Source (ALS) in Lawrence Berkeley National Laboratory (LBNL). The energy resolutions of the incoming and outgoing X-rays were 0.2~0.3 eV. For the calibrations of the monochromator and spectrometer, *h*-BN, B_2O_3 , HOPG and natural diamond were used as the standard samples.[12, 13, 14] Although all the samples are polycrystals, there is a possibility of orientation. In order to check the orientation and the surface π -resonant state reported in some borides, polarization (angle) dependencies of XAS and XES were measured. There are no essential differences in XAS and XES spectra among those with different angles, which suggests that there is no orientation and any borides showing the surface π -resonant state in these samples.

III. RESULTS AND DISCUSSIONS

A. B-K XAS and XES of doped diamond film

Figure 1 shows B-K XAS and XES spectra of B- and BN-diamonds. In both compounds, clear metallic states of B-2p are observed, in which both the Fermi level are the same with each other to be of 185.3 eV measured from B-1s core level. There is a pseudo-gap state between 187 and 190 eV, and the intensity steeply increases with an increase of energy with the threshold of 190.5 eV. It is

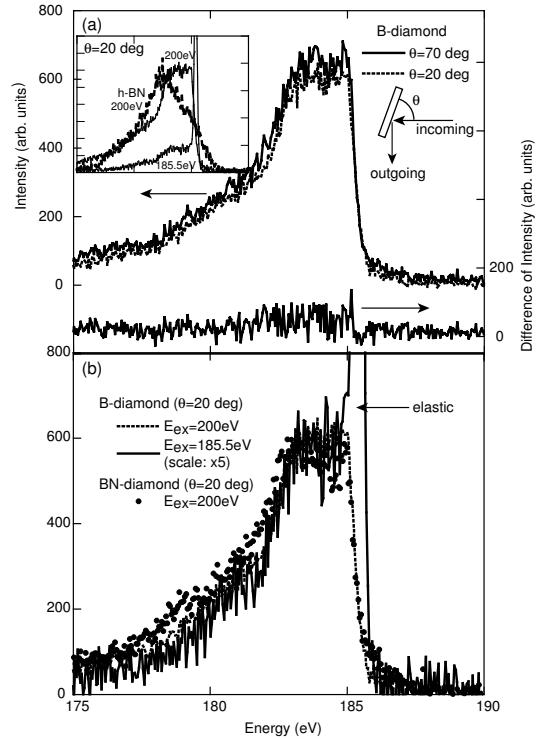


FIG. 2: B-K XES spectra of B- and BN-diamonds. (a) The incident-angle dependence of B-diamond. The inset shows excitation-energy dependence and shows B-K XES spectrum of *h*-BN. (b) The excitation-energy dependence of B-diamond, in which the spectrum with E_{ex} of 185.5 eV being magnified 5 times. The spectrum of BN-diamond with E_{ex} of 200 eV is also shown.

noticed that there is no sharp peak at 192 eV (* in Fig. 1) which corresponds to the surface π -resonant state of some borides, *h*-BN and B_2O_3 . This means there is no trace of these borides in these diamond samples.

Figure 2 shows angular and energy dependence of B-K XES spectra of B- and BN-diamonds. Figure 2(a) shows two B-K XES spectra of B-diamond with the different incident angle θ of 70° and 20° . The excitation energy, E_{ex} , is 200 eV. These two spectra coincide each other, which indicates that there is no orientation of this sample. The most important point is the observation of the clear Fermi edge in both samples with the same threshold at 185.0 eV in consistent with B-K XAS spectra. The inset viewgraph shows B-K XES spectrum with E_{ex} of 185.5 eV which corresponds to the sharp state near the Fermi level in B-K XAS spectrum (Fig. 1). In the inset, the spectra of *h*-BN with E_{ex} of 200 eV is also plotted. The bonding in *h*-BN is ideal sp^2 between B and N having a peak at around 182~183 eV. The observed B-K XES spectra of B-diamond differ from that of *h*-BN, but it is hard to say that this spectra is due to sp^3 of B in diamond from these results only. Figure 2(b) shows detailed excitation-energy dependence of B-diamond. For the spectrum with E_{ex} of 185.5 eV, the elastic (intense) peak at is observed. Then we magnified the spectrum

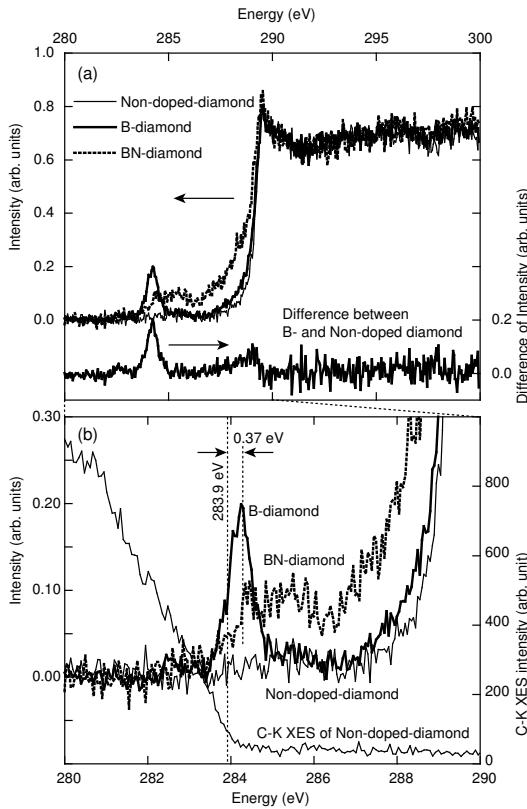


FIG. 3: C-K XAS spectra of B-, BN- and Non-doped-diamonds. (a) overall features of those spectra, (b) detailed spectra of the in-gap states. The XAS and XES of non-doped diamond are also shown. The dashed lines indicate the top of the valence band of non-doped diamond and the impurity level excepted from the activation energy of BN-diamond, respectively.

with E_{ex} of 185.5 eV 5 times in Fig. 2(b). The detailed features of these spectra in the energy region of $E \leq 184$ eV agrees well with each other. This means that all B- $2p$ has an unique electronic structure. Furthermore the spectrum of BN-diamond shows almost same form, which means there is no B concentration dependence in these doping region.

B. C-K XAS of doped diamond film

Figure 3 shows the C-K XAS spectra of B-, BN- and non-doped-diamonds. Figure 3(a) shows the overall features of C-K XAS spectra. The spectrum of non-doped-diamond (thin solid line) shows clear gap state with $E \leq 289.1$ eV which corresponds to the bottom of the conduction band (C.B.). On the other hand, the spectra of B- and BN-diamonds show in-gap states. For B-diamond (thick solid line), only one peak at 284 eV is observed as the in-gap state. The threshold energy of this peak is estimated to about 283.9 eV which is consistent with the energy expected from both the observed bottom of C.B.

(289.1 eV) and the band gap of non-doped diamond. In Fig. 3(a), the difference between B- and non-doped diamonds is also shown. It is clearly seen that the 1-at% B in diamond makes a metallic state in C- $2p$ PDOS. But for BN-diamond (dotted line), the threshold energy shifts higher a little. Figure 3(b) shows detailed in-gap states and shows the edge of C-K XES of non-doped diamond. The threshold energy of the impurity state in XAS of B-diamond, 283.9 eV, is agreement with the edge energy in C-K XES of non-doped diamond (the top of the valence band, E_v). It is noted that all the profiles of normal C-K XES of B-, BN- and non-doped diamond are almost same (see section III C). In contrast to the metallic B-diamond, BN-diamond seems to has a small gap. For this semiconducting sample the activation energy, E_a , of 0.37 eV was measured from the temperature dependence of the conductivity.[9] Then, the shift of 0.3~0.4 eV between metallic and semiconducting samples is consistently explained by the small gap with E_a of 0.37 eV. In other words, 0.1-at% B makes a shallow level near the valence band with E_a of 0.37 eV. In addition, a broad in-gap state spreads over the gap is observed in BN-diamond. It is reported that nitrogen-dopant makes several deep levels in diamond[10] and the present spectra are similar to the reported C-K XAS spectra for graphite-carbon nitride system.[15] Then this broad in-gap state is ascribed to N-dopant.

C. C-K XES of doped diamond film

Figure 4(a) shows the C-K XES spectra with E_{ex} of 284 eV and 300 eV. The spectrum with E_{ex} of 300 eV (dotted line) is almost same as the spectrum of the non-doped-diamond.[12] This is consistent with the band calculation results.[16] This agreement between doped and non-doped diamond suggests that the host C-1s core level does not change by B-doping within the experimental error. However, the spectrum with E_{ex} of 284 eV (thick solid line) shows a sharp peak at about 284 eV (elastic peak) and a broad tail toward the low energy side. Figure 4(b) shows the subtraction of the elastic peak from the spectrum. The elastic peak was assumed to be gaussian with FWHM of 0.6 eV.[17] The result of the subtraction of the elastic peak is essentially same as before the subtraction because the width of elastic peak is narrow. Because the unoccupied state, a peak at 284 eV is observed only in B-doped-diamond, the XES spectrum with E_{ex} of 284 eV is a represent of the PDOS of the carbon atom hybridized with dopant B, i.e., nearest neighboring (N.N.) carbon from boron. Because it is difficult to study the electronic structures of dopant (dilute) boron and the neighboring carbon atoms using band calculation, calculations were performed by, DVX α method.[18], a cluster calculation method.

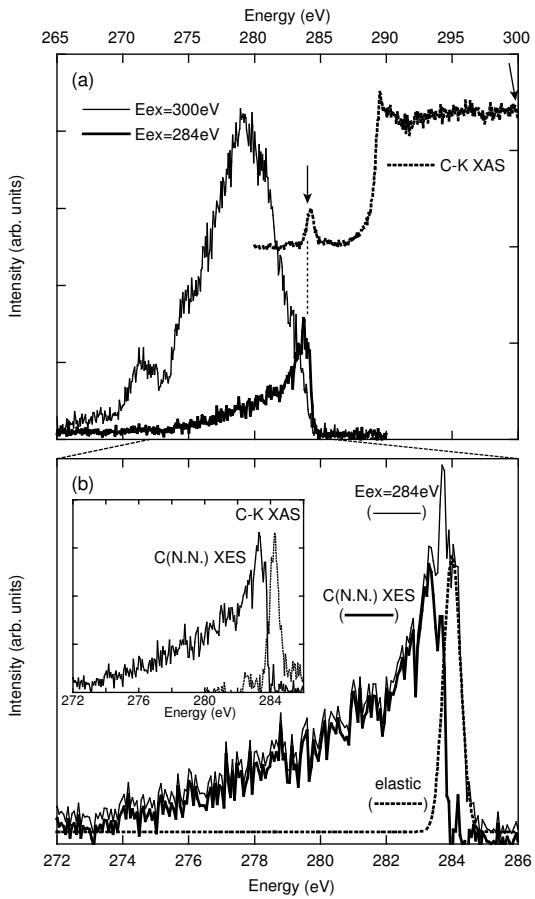


FIG. 4: C-K XES spectra of B-diamond: (a) XES spectra with E_{ex} of 284 eV (near the Fermi energy) and of 300 eV. C-K XAS spectrum of B-diamond is also shown (two arrows indicate two E_{ex} positions). (b) C(N.N.) XES spectra derived from the subtraction of the elastic peak from observed XES spectra with E_{ex} of 284 eV (near the Fermi energy). The inset shows C(N.N.) XES and C-K XAS spectra.

D. DVX α cluster calculation

The program SCAT[18] was used for DVX α calculation. Because the samples are covalent, Madelung potential was not taken into account. It is also known that an average of PDOS's of a few atoms near the center of the large cluster reproduces well experimental results. In the present work, we calculated the PDOS's for non-doped-diamond, and two doped diamond cases where boron occupies the interstitial site and substitute's carbon site. The typical cluster size is about 200 atoms, a limitation due to the memory size of the program. First, PDOS of non-doped cluster model, C₁₈₄, was calculated and the results were compared with the experimental data and the band calculations. Although the Fermi levels in both the calculations and observation are not agreed exactly, the overall feature of the PDOS's are in agreement with each others. For the B doped diamond case, typical cluster models of C₁₇₄BH₁₆ and C₁₈₄BH₁₂ were used

for substitutional and interstitial cases, respectively. In these cases, the non-doped models, C₁₇₅H₁₆ and C₁₈₄H₁₂ were also applied and the results were confirmed to be same with that of C₁₈₄. In both B-doped cluster models, boron atom is always set at the center of the clusters. In these large clusters, an effect of H-termination is found to be negligible for the PDOS's of inner C or B atoms. It is noted that a few in-gap states are appeared even in the non-doped case. It might be ascribed to the surface states. Then in the present DVX α results, the origin of the energy is set to the maximum energy of the electron in the occupied states except the meaningless surface states, i.e., the energy is measured from the top of the valence band (V.B.), E_V .

The results are shown in Fig. 5. Figure 5(a) shows experimental XES spectra of B-K with E_{ex} of 200 eV, C-K with E_{ex} of 284 eV and C-K with E_{ex} of 300 eV of B-diamond, corresponds to PDOS of B-2p, C(N.N.)-2p and host C-2p, respectively. B-K XAS spectra of B-diamond near the Fermi level are also shown (red dashed line). The horizontal axes for B-K and C-K are shifted in order that the Fermi level is in agreement with each other. One can see that there is a good agreement in between B-2p and C(N.N.)-2p PDOS, which means strong hybridization between these orbitals. Figures 5(b) and (c) show the results in substitutional and interstitial cases. The origin of the energy in DVX α is set to the maximum energy of the electron in the occupied states, i.e., top of the V.B. The PDOS of C(N.N.)-2p (blue line) is derived as averaged PDOS of four N.N. carbon atoms [the four blue balls in the inset in Figs. 5(b) and (c)]. The PDOS of host C-2p (black line) is the averaged one of a few carbon atoms near the center of the cluster but far from the dopant boron, which is in good agreement with the result of non-doped cluster, C₁₈₄. All the calculated PDOS's are convoluted using gaussian function with the experimental width. In the substitutional case [Fig. 5(b)], PDOS of B-2p (red line) shows a large peak around $E - E_V = 0 \text{ eV}$, and PDOS of C(N.N.)-2p possesses a main peak around $E - E_V = -3.8 \text{ eV}$. It is worth while to notice that the considerable amounts of state around E_V are appeared in both PDOS's of B-2p and C(N.N.)-2p. It is consistent with the experimental results that the observed PDOS's of B-2p and C(N.N.)-2p also shows main states (peak) in higher energy side from the PDOS of host C-2p. Furthermore, the broad-beat structures of the B-2p PDOS's tail in the low energy side agrees with those of C(N.N.)-2p PDOS, which is consistent with the strong hybridization between dopant B-2p and C(N.N.)-2p observed experimentally [inset of Fig. 4(b) and Fig. 5(a)]. The result in the substitutional case is consistent with the experimental one. On the other hand, in the interstitial case, both the PDOS's of B-2p and C(N.N.)-2p shift and broaden toward the low energy side. Especially large in-gap states for both B-2p and C(N.N.)-2p PDOS's are appeared with the threshold energy of about $E - E_V \sim +3 \text{ eV}$. There are almost no states near the E_V , which does not support the experimental results. These results of

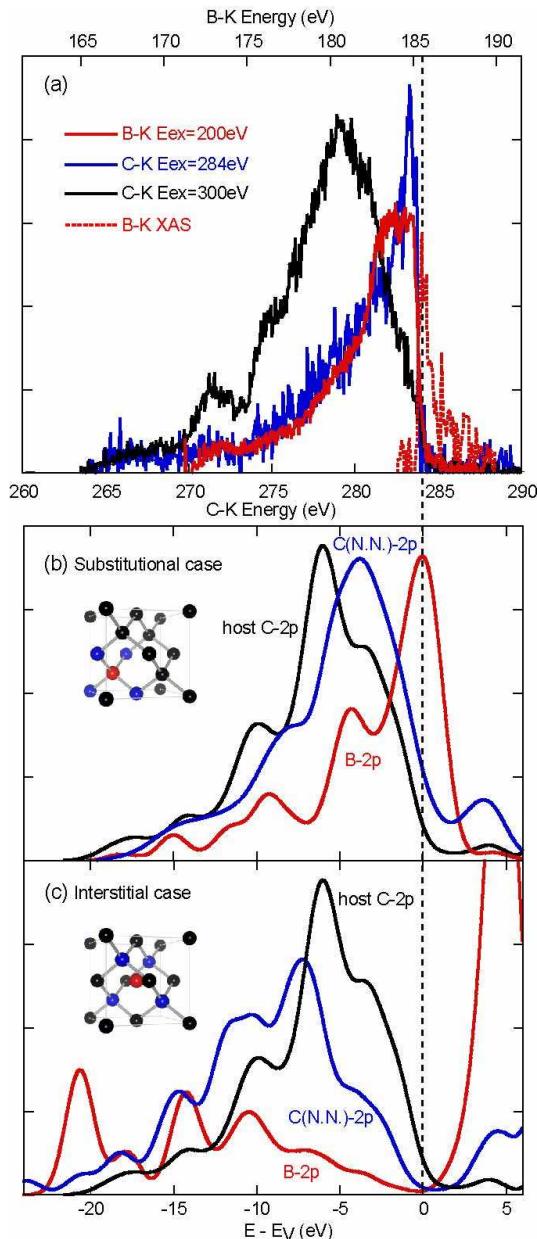


FIG. 5: Comparison of observed B-K XAS and XES, and C-K XES spectra with DVX α simulations. (a) Observed XAS and XES spectra, (b) DVX α -results of substitutional case, and (c) DVX α -results of interstitial case. In the inset pictures of (b) and (c), red and blue ball represent boron and N.N. carbon atoms, respectively.

DVX α suggest that dopant boron replace the carbon sites in these concentration region consistently with the pre-

vious report.[7]

IV. CONCLUSIONS

X-ray absorption (XAS) and emission (XES) spectra at the B-K and C-K edges have been performed on metallic (~ 1 at% B) and semiconducting (~ 0.1 at% B and N) doped-diamond films. Both B-K XAS and XES spectra show metallic partial density of states (PDOS) with the Fermi energy of 185.3 eV, and there is no apparent boron-concentration dependence in contrast to the different electric property. In C-K XAS spectrum of metallic B-diamond, the impurity state ascribed to boron is clearly observed near the Fermi level. The Fermi energy is found to be almost same with the top of the valence band of non-doped diamond, E_V , 283.9 eV. The C-K XAS of semiconducting BN-diamond shows both the B-induced shallow level and N-induced deep-and-broad levels as the in-gap states, in which the shallow level is in good agreement with the activation energy ($E_a=0.37$ eV) estimated from the temperature dependence of the conductivity, namely the change in C-2p PDOS of impurity-induced metallization is directly observed. The electronic property of these diamonds is mainly attributed to the electronic structure of C-2p near the Fermi level. The observed XAS and XES spectra are compared with the DVX α cluster calculations. The DVX α result supports the strong hybridization between B-2p and C-2p observed in XAS and XES spectra, and suggests that borons in diamond occupy the substitutional site in the present doping range between 0.1at% B and 1at% B in diamond, rather than interstitial site.

Acknowledgment

We express our thanks to Dr. Y. Muramatsu of Japan Atomic Energy Research Institute (JAERI), Prof. K. Kuroki of University of Electro-Communications and Prof. T. Oguchi of Hiroshima University for useful discussions. J.N. wishes to acknowledge to Dr. J.D. Denlinger of the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory (LBNL) for the experimental support. This work was performed under the approval of ALS-LBNL, proposal No. ALS-00931. ALS is supported by the Director, Office of Science, Office of Basic Energy Sciences, Materials Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098 at LBNL.

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